

Characterization of Manganese Oxide Powder Processed by Gas Condensation Method.

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INTRODUCTION

The manganese oxide powder is considered to be important cathode material in the lithium ion secondary battery. The preparation of the finer manganese powder is directly related to the increase of cathode surface area and is consequently able to improve the capacity of static electricity. Manganese powder processing by the gas condensation method was tried to make from several nano meter to decades nano meter sized powder and the near edge x-ray absorption fine structure (NEXAFS) study on the powders was done for the analysis of the oxidation degree depending on the processing condition and the oxidation heat treatment afterwards.

The gas condensation method is one of the unique ultra fine powder making processes and has more advantage than the gas evaporation method since the powder produced by the former method shows finer size and more narrow size distribution[1,2]. There are several other methods for making nano sized ultra fine powders such as mechanical crushing by ball milling, deposition from the salt solution, sprayed thermal decomposition, laser heating and clustering, sol-gel processing etc.[3-6]. However, gas condensation and gas evaporation methods are favorably studied since the powder surfaces are cleaner and less stained by the contamination.

The gas condensation method has two processes, that is, metal powder condensation process and oxidation process. In the metal powder condensation stage, low pressure inert gas is introduced into the vacuum melting chamber and the vaporized metal gas of atomic unit is clustered to each other and condensed to ultra fine size powder by contacting cold gas. In the second step, low pressure oxygen gas is introduced to the chamber and the fine metal powder is oxidized thereafter. Subsequent heat treatment in air atmosphere is done for the further oxidation. First NEXAFS study of the nano sized powder surfaces will be presented and this will define the final oxidation state of the metal powder.

EXPERIMENTAL

Three kinds of nano sized ultra fine manganese powders were produced by melting the pure manganese metal (99.99%) at the temperature of 1150°C in vacuum (1×10^{-6} Torr), evaporation by introducing low pressure helium gas 1 Torr, 10 Torr and 100 Torr respectively and subsequent holding at a pressure of 300 Torr (firstly filling with helium gas 100 Torr and then filling oxygen gas to 300 Torr) for 3 hours in the cylindrical chamber with 30cm diameter and 55cm height[7]. Melting was done by resistance heating in tungsten boat. The different helium gas pressure during the gas condensation process gave variations in the powder size and oxidation degree.

Three ultra fine manganese powders were heated in air atmosphere to the temperature of 520°C at a heating rate of 10°C per minute since they showed reaction peaks in the range of 200°~300°C and

around 500°C in the DSC curves. On the three raw powders made with different helium pressure and three heat treated powders, NEXAFS analysis has been performed using the photo-emission electron microscope located at beam line 8.0 of ALS. Each powder was put on carbon tape and attached by rubbing the powder repeatedly and spreading as thin as possible. Carbon tape held the powder stictly was fixed on the sample holder. The X-ray diffraction of the same powder samples has been also done and compared to NEXAFS results.

RESULTS and DISCUSSION

Manganese oxide powders made by gas condensation method had ultra fine size and relatively narrow particle size distribution observing the size and morphology by transmission electron microscope. Clustered round particles with similar size showed size increasing trend from about 10 to 40 nm size with increase of helium gas pressure from 1 Torr to 100 Torr during evaporation and condensation process. This indicates that pressure increase retarded evaporation rate and gas convection current in the chamber and accelerated the impingement of helium and metal gas and consequently brought about the growth of the condensed particles.

For the three ultra fine manganese oxide powders, structure analysis by x-ray diffraction was done and β -Mn, MnO and Mn_3O_4 were observed respectively in every powder. β -Mn peak was the strongest intensity in every powder and increased with increase of helium gas pressure. Differential scanning calorimetry from 0 to 900°C at the heating rate of 10°C per minute was applied for three manganese oxide powder and two clear peaks were found, that is, one peak between 200°C and 300°C and the other peak between 500°C and 520°C respectively. These suggest that some kinds of oxidation reaction occurred below 520°C. Therefore, heat treatment to the temperature of 520°C at the heating rate of 10°C was performed for three manganese oxide powders and x-ray diffraction analysis was followed.

X-ray diffraction pattern comparison between the raw and heat treated powders were summarized for the three different manganese oxide powders in Fig.1. The manganese oxide powder processed by 1 Torr helium atmosphere showed higher oxidation to Mn_2O_3 while other two powders processed by 10 Torr and 100 Torr helium atmosphere exhibited less oxidation only to Mn_3O_4 . This means that small sized powder oxidized to higher oxidation degree and surface oxidation is retarded by the insufficient oxidation of powder core.

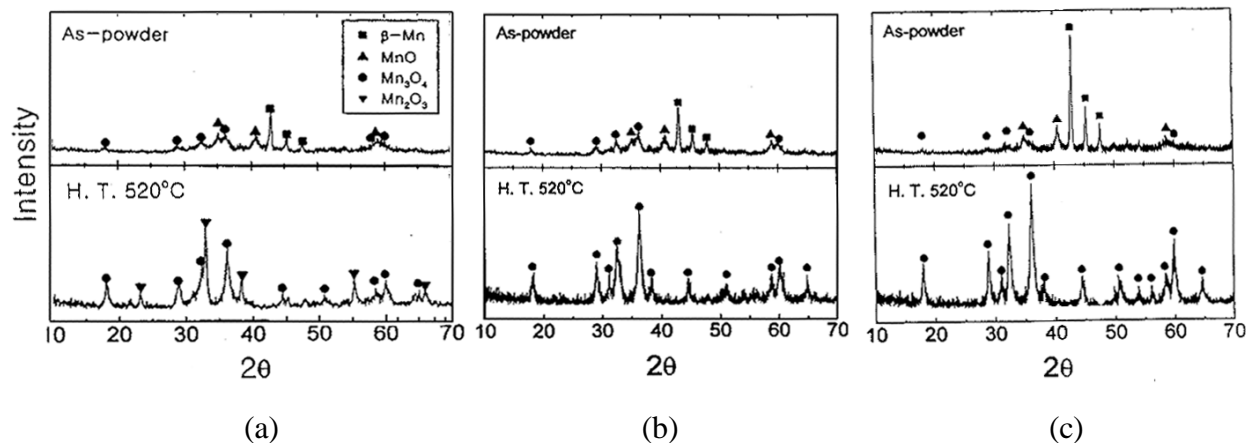


Fig.1. X-ray diffraction pattern comparison of the three different manganese oxide powders before and after heat treatment at 520°C. (a) manganese oxide powders processed by 1 Torr helium gas, (b) those processed by 10 Torr helium gas and (c) those processed by 100 Torr helium gas.

Surface oxide was analyzed by L_3 -edge absorption of Manganese NEXAFS spectra for the raw manganese oxide powders and the heat treated ones. In the photo-emission electron microscope of beam-line 8.0.1, powder morphology with different size was observed and the relevant NEXAFS spectra were obtained. In Fig. 2 three sets of Mn L_3 NEXAFS spectra were summarized depending on the helium gas pressure and those of raw powder and heat treated one were compared in each plot.

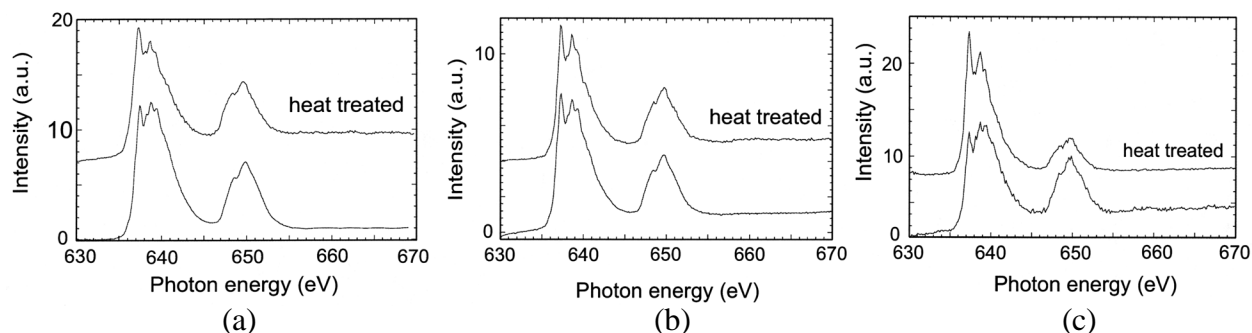


Fig. 2. L_3 NEXAFS spectra of manganese oxide powders synthesized by gas condensation method. (a) powders synthesized by helium gas pressure 1 Torr, (b) powders synthesized by helium gas pressure 10 Torr and (c) powders synthesized by helium gas pressure 100 Torr.

The L_3 NEXAFS spectra showed that oxidation occurred more than MnO in all the powders. In these NEXAFS results, sharp peaks of 637eV and 650eV were clearly and similarly shown in every powder. All the three raw powders had nearly the same peaks and this means that the surface of the powders are covered with Mn_3O_4 [8]. Main change occurred in the complicated peaks between 638 eV and 639.5 eV in the shape and height. These change indicates the oxidation of Mn_3O_4 to Mn_2O_3 [8]. The powder processed by 1 Torr helium gas showed more pronounced oxidation through heat treatment. This means that the oxidation of the smaller size powder reached early to Mn_2O_3 state while other bigger size powders remained as Mn_3O_4 state. The NEXAFS of Fig.2 and the x-ray diffraction results of Fig.1 show that the oxidation reaction occurred from surface to interior and β -Mn and MnO layers remained in the core of the decades nano particle and also the surface layer of Mn_2O_3 was not thick enough to detect easily by NEXAFS.

CONCLUSION

Gas condensation method was first applied in making ultra fine manganese oxide powder and controlled-size powders from about 10 to 40 nm were obtained by ruling the helium gas pressure from 1 to 100 Torr. These powders were heat treated at the temperature of 520°C and the oxidation degree was analyzed by x-ray diffraction and L_3 edge Mn NEXAFS. Oxidation occurred during gas condensation process but β -Mn and MnO layer remained in the core of the decades nano meter sized powder. More oxidation at the temperature of 520°C made the powder surface Mn_3O_4 and Mn_2O_3 . The Mn NEXAFS studies for the nano sized manganese powder revealed surface oxidation results consistent with x-ray diffraction. Further study on the nano sized powder characterization is needed for better understanding of the oxidation reaction and powder surface properties.

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